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(71) 出願人 000005108

株式会社日立製作所

東京都千代田区神田駿河台四丁目6番地

(72) 発明者 川澄 達一

東京都青梅市藤橋888番地 株式会社日立  
製作所青梅工場内

(72) 発明者 宇野 良男

東京都青梅市藤橋888番地 青梅産業株式  
会社内

(72) 発明者 稲田 暁勇

東京都青梅市藤橋888番地 株式会社日立  
製作所青梅工場内

(74) 代理人 弁理士 小川 勝男

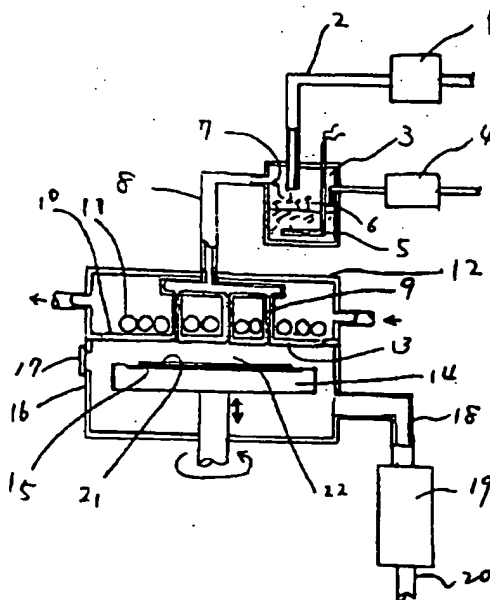
(54) 【発明の名称】 洗浄方法

(57) 【要約】

【目的】 レジスト等の有機物の灰化除去の均一性能の改善しスループット向上を図る

【構成】 予め蒸発潜熱を持った状態の水蒸気をオゾンとともに供給するため加熱できる水蒸気供給水槽を備える。

【効果】 水分を直接ウェハにあてないので蒸発潜熱によるウェハの過度の冷却がない。オゾンに水分を含有させる水を加熱するので蒸発潜熱によって水槽の冷却並びにオゾンガスの冷却がないのでウェハを部分的に冷却せず、除去速度分布が均一になりスループットが改善出来る。



とを避けている。ステージへのウェハの密着性を良くするためにウェハは、前記石英製の薄い平板15を介して真空吸着する。

【0013】該ステージ14へのウェハ21のローディング、アンローディングは、ステージを包囲する処理室16の一方に設けた開閉可能な搬送窓17を介して搬送ロボット（図示しない）により行う。この時ステージは、ロボットのウェハ吸着面がウェハの裏面に入るように上下駆動する。また、前記複数のガス供給ノズルから供給する反応ガスをウェハ面上に均一に且つ高速で通過させると同時に、ライフタイムの短い活性酸素原子を有効にウェハ面に与えるために、ウェハ面と前記合成石英の平板の精密な面とのあいだの前記反応ガスを流すガスフローギャップ22を処理中極めて小さく制御する。処理中ウェハ21はステージの回転によって回転しながら紫外線の照射および反応ガスの供給を全面にほぼ均等に受けることができる。

【0014】前記処理室16には、残存するオゾン进行を排気するダクト18を配置しさらに該残存オゾン进行を分解器19により酸素に変えて空気とともに大気へ放出する。

【0015】

【発明の効果】本発明により、添加する水分がウェハ面上に当たる前に蒸発潜熱を有していること、且つオゾンが水分の蒸発潜熱を奪われた水によって冷却されることがないのでこれら反応ガスの供給によってウェハ表面の温度が部分的に極端に冷却されることがないので均一なレジスト除去処理ができスループットの改善ができる効果がある。

【図面の簡単な説明】

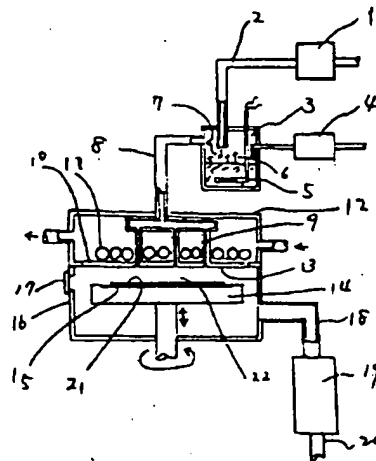
【図1】図1は、本発明の一実施例を説明するための概念図

【符号の説明】

1：オゾン発生機、2：A配管、3：水蒸気供給水槽、4：水定量補給装置、5：ヒータA、6：水蒸気（または過酸化水素含有水蒸気）、7：オゾンの気流、8：B配管、9：ガス供給ノズル、10：合成石英の平板、11：低圧水銀放電灯、12：ランプハウス、13：研磨面、14：ステージ、15：石英製の薄い平板、16：処理室、17：搬送窓、18：ダクト、20：ダクト、21：ウェハ、22：ガスフローギャップ。

【図1】

図 1



## 【特許請求の範囲】

【請求項1】 オゾンと紫外線の作用によって有機物を分解し、気化して除去する洗浄方法であって、オゾンとともに蒸発潜熱を有したガスの状態の水または、過酸化水素を被処理物の表面に供給することを特徴とした洗浄方法

## 【発明の詳細な説明】

【0001】 本発明は、ガラスやシリコンウェハの洗浄、マスクとして使用したホトレジストなど有機物をガス状にして洗浄、除去する方法に係る。

## 【0002】

【産業上の利用分野】 本発明の方法は、光学ガラスや液晶用ガラスの洗浄、半導体装置製造等における加工表面の有機物の汚れや、マスクとして使用した後のレジストの除去に利用される。

## 【0003】

【従来の技術】 オゾンの分解により生成された活性酸素原子によって有機物を灰化除去することは、たとえば特開昭58-15939号に示されているように古くから知られている。また、その除去性能を向上させるために例えば、特公平1-179327号に示すようにオゾンと共に水を供給することが知られている。しかしながら上記公知の、特公平1-179327号においては供給する水分が被処理物の表面から蒸発潜熱を奪い被処理物の表面温度を低下させる点について考慮されておらず、またオゾン在水中に通ってきた水蒸気をオゾンとともに供給する場合において水中から水の蒸発潜熱が奪われ水温が低下し水蒸気の量が減少すること及びオゾンガスの冷却が生じてることについて配慮されていなかった。このような点は、特に低温処理においては被処理物表面の部分的な冷却を生じ除去速度分布におおきな不均一が生ずるという問題があった。

## 【0004】

【発明が解決しようとする課題】 本発明の目的は、供給水分が蒸発潜熱を有した状態でかつその量を常に一定に供給することと、供給ガスの冷却によって被処理物の表面の温度分布に大きな差が生じることを防止することによって、とくに低温処理において除去性能を向上することにある。

【0005】 オゾンと紫外線による洗浄方法においては、200℃程度以下での低温での処理における供給ガスの吹き付けによる被処理物表面の冷却は、除去速度分布の均一性を悪くしスルーブットの面で無視できない。従って供給ガスの加熱が考えられるが、オゾンは200℃程度の加熱によっても熱分解しやすいこと、大気圧では分解して得られた活性酸素原子の寿命は極めて短い性質があるために水分を含有させる部分での過度の加熱は不适当でありオゾンの加熱には細心の注意が必要である。即ち、被処理物表面から遠い位置で過度に加熱したときは活性酸素原子の状態では被処理物表面に到達しない

と同時に被処理物表面上でのオゾンの濃度を低下させてしまい除去速度の低下を招く。

## 【0006】

【課題を解決するための手段】 オゾンに水分を含有させる前または、その部分において供給水分の量を蒸発させるに必要な潜熱に匹敵する熱量を外部から供給する。この蒸発した水蒸気をオゾンの気流にのせ十分に混合させて被処理物の表面に供給する。

## 【0007】

10 【作用】 供給する水蒸気は、予め蒸発潜熱を持っているので被処理物から蒸発潜熱を奪って被処理物の温度を過度に低下させることはない。また、オゾンも蒸発潜熱を奪われて冷えた水によって冷却されないで被処理物の表面温度分布を過度に乱さず処理速度分布の改善ができる。

## 【0008】

【実施例】 半導体装置の製造においてウェハ上でマスクとして使用した後のレジストの膜を除去する方法として、大気圧中でレジストに紫外線とオゾンとを作用させて有機物であるレジストをCO<sub>2</sub>、H<sub>2</sub>O等のガスに分解して除去する例について説明する。図1、上記一実施例を説明するための装置の概念図である。

【0009】 原料酸素ガスを石英製の円筒を2重にしてその間の狭い空間に流し、2重の筒の間で放電させオゾン発生機1によりオゾンを生成する。該オゾンをA配管2によって水蒸気供給槽3に導入する。該水蒸気供給槽には、定量補給装置4によって純水、或いは過酸化水素が供給され、さらに該水蒸気供給槽4は内部の水温を一定に保持するようにヒータA5を内蔵している。該水蒸気供給槽4の水面より蒸発した水蒸気6は、該水蒸気供給槽4に導入されたオゾンの気流7に乗ってB配管8によって複数のガス供給ノズル9に供給する。該B配管8は、供給した水蒸気が結露しない温度に保温する。

【0010】 前記の複数のガス供給ノズル9は、合成石英の平板10に貫通溶接してあり、各ノズル9は、回転中心を避け且つ、それぞれが同一回転半径上にないように配置する。

【0011】 前記合成石英の平板10のノズル配置側に平面上で折り曲げて平面照射出来るようにした合成石英管を発光管とした低圧水銀放電灯11を配置する。該低圧水銀放電灯11は、アルマイト仕上げを施したアルミニウム製のランプハウス12に収納する。該ランプハウス12の中に窒素ガス等の不活性ガスを導入置換して発光管の周りでオゾンが発生することを防止する。

【0012】 前記合成石英の平板10のノズル配置側とは反対の面13（研磨面）は、研磨により精密な平面度に仕上げする。該精密な研磨面13の前方に回転、上下可能な加熱ヒータ内蔵のステージ14を配置する。該ステージ14のウェハ搭載部分は、石英製の薄い平板15を配置しウェハと金属ステージ14とが直接接触するこ

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(71) Applicant: 000005108  
Hitachi, Ltd.  
4-6 Kanda Surugadai  
Chiyoda-ku, Tokyo

(72) Inventor: Kenichi Kawazumi   
Inside the Oume Plant of Hitachi, Ltd.  
888 Fujihashi  
Oume City, Tokyo

(72) Inventor: Yoshio Uno  
Inside the Oume Plant of Hitachi, Ltd.  
888 Fujihashi  
Oume City, Tokyo

(72) Inventor: Akiisa Inada  
Inside the Oume Plant of Hitachi, Ltd.  
888 Fujihashi  
Oume City, Tokyo

(74) Agent: Katsuo Ogawa, Patent Attorney

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Specifications

(54) <Name of Invention>

Cleaning Method

(57) <Abstract>

### <Purpose>

This invention is designed to improve the uniformity of the ashing process in which organic matter such as resist is removed in order to increase the level of throughput.

### <Constitution>

A water tank that can be heated for the purpose of delivering water vapor is provided so that ozone can be delivered along with water vapor that already contains the latent heat of evaporation.

### <Effect>

Since moisture does not make direct contact with the wafer, there is no excessive cooling of the wafer due to the latent heat of evaporation. Since water that is used to introduce moisture into the ozone is heated, there is no cooling of the water tank or the ozone gas due to the latent heat of evaporation, and for this reason, no partial cooling of the wafer occurs. As a result, uniformity is achieved with regard to the velocity distribution of removal, making it possible to improve throughput.

Figure 1

## <Claims>

### <Claim 1>

A cleaning method is characterized by a removal process in which ozone and ultraviolet light are used to decompose and vaporize organic matter. Specifically, water or hydrogen peroxide is delivered in the form of a gas that contains latent heat of evaporation onto the surface of a material that is being treated.

## <Detailed Description of the Invention>

### <0001>

This invention is related to a method for cleaning glass or silicon wafers, wherein a masking process is used and organic matter such as photoresist is converted into a gas-form so that it can be cleaned away from said wafer.

### <0002>

### <Industrial Field of Application>

This invention is used in the removal of resist following a masking process, or in the removal of organic contaminants from a processed surface during the manufacture of semiconductor devices or when cleaning is conducted for optical glass or other glass materials used for liquid crystals.

### <0003>

### <Prior Art>

Methods for conducting ashing removal of organic matter through the use of active oxygen atoms that are created when ozone is decomposed have been known for many years, as indicated in Patent No. S58-015939 [1983]. Furthermore, efforts to improve removal performance, as indicated in Patent No. H01-179327 [1989], have become known in which ozone is delivered along with water. However, in the case of the aforementioned Patent No. H01-179327, one point that is not considered is the fact that the moisture that is delivered robs the surface of the material being treated of the latent heat of evaporation, causing a drop in the surface temperature of the treated material. Another point not considered is that in the case where water vapor that has been obtained by passing ozone through water is delivered along with ozone, the latent heat of evaporation is stolen from within the water, causing a drop in the water temperature and a reduction in the amount of water vapor as well

as cooling of the ozone gas. Particularly in the case of low-temperature treatment processes, these points lead to partial cooling of the surface of a treated material, resulting in a significant level of non-uniformity with respect to the velocity distribution of removal.

<0004>

#### <Problem to Be Solved by the Invention>

The purpose of this invention is the delivery of moisture in a state in which it contains latent heat of evaporation and in a manner in which the delivery amount is usually constant. This is necessary in order to prevent a significant amount of variance in temperature distribution along the surface of a treated material such that the removal performance can be improved, particularly in the case of low-temperature treatment processes.

<0005>

In the case of cleaning methods conducted through the use of ozone and ultraviolet light, it cannot be ignored from the standpoint of throughput that the cooling of the surface of a material being treated due to the blowing of the gas as it is delivered during low-temperature treatments of 200°C or lower has an adverse effect on uniformity with respect to the velocity distribution of removal. Accordingly, it is possible to consider heating the gas, but due to the fact that ozone can easily undergo thermal decomposition when heated at a temperature of approximately 200°C, as well as the fact that the lifetime of active oxygen atoms that are obtained through decomposition at atmospheric pressure is extremely short, excessive heating of areas in which moisture has been introduced is unsuitable, and therefore the heating of ozone needs to be treated with the greatest possible care. In short, when excessive heat is applied from a position that is far away from the surface of the material being treated, it will not reach the surface in the form of active oxygen atoms, and at the same time, this will end up causing a drop in the concentration of ozone along the surface, which will lead to a drop in the velocity of removal.

<0006>

#### <Means for Solving the Problem>

Before moisture is introduced to the ozone, an amount of heat that matches the latent heat required for evaporation of the moisture to be delivered is provided externally. This evaporated water is introduced into the



ozone stream and sufficiently mixed with the ozone before it is delivered to the surface of the material being treated.

<0007>

<Operation>

Since the water vapor that is delivered already contains latent heat of evaporation, there is no robbing of the latent heat from the treated material, and excessive reduction in the temperature of the material is prevented. Furthermore, since there is also no cooling of the ozone due to any loss of latent heat within the water, the surface temperature distribution of the material being treated is not excessively disturbed, which makes it possible to improve the velocity distribution of the treatment.

<0008>

<Embodiment>

As a method for removing a resist film after a mask has been used on a wafer during the production of a semiconductor device, ultraviolet light and ozone are applied to the resist under atmospheric pressure conditions, and the resist, which is a form of organic matter, is decomposed to form a gas such as  $\text{CO}_2$  or  $\text{H}_2\text{O}$ . Figure 1 is a conceptual drawing of a device that is provided for the sake of explaining this embodiment.

<0009>

A raw material oxygen gas flows through the narrow space between dual cylinders made from quartz, and ozone is formed by the ozone generator 1 when an electrical discharge is provided between these dual cylinders. This ozone is then introduced into the water vapor delivery tank 3 via the A-pipe 2. Purified water or hydrogen peroxide is then delivered to said water vapor delivery tank by means of a fixed-quantity supply device 4, and a heater A5 is built into said water vapor delivery tank 4 [sic; should be 3] for the sake of maintaining a constant water temperature. The water vapor 6 that rises from the water surface within said water vapor delivery tank 4 [sic; should be 3] enters the air stream 7, which contains the ozone that has been introduced into said water vapor delivery tank 4 [sic; should be 3], and is then sent to multiple gas delivery nozzles 9 via the B-pipe 8. Said B-pipe 8 is maintained at a temperature that prevents condensation of the water vapor that has been delivered.

<0010>

The multiple gas delivery nozzles 9 noted above are welded to a flat plate 10 made of composite quartz such that they are allowed to pass through the plate, and each nozzle is placed such that it avoids the center of rotation and is not located at the same turning radius of any of the other nozzles.

<0011>

A bend occurs at the plane surface of the aforementioned flat plate 10 where the nozzles are located, and low-pressure mercury lamps 11 are installed in the form of luminescent tubes made of composite quartz in order to make it possible to provide planar irradiation. Said low-pressure mercury lamps 11 are stored within a lamp housing 12 made of aluminum that has undergone alumite finishing. An inactive gas such as nitrogen is introduced into said lamp housing 12 to prevent ozone from being generated along the circumference of the luminescent tubes.

<0012>

The surface 13 (polished surface) on the opposite side of the flat plate 10 where the nozzles are located is polished to a fine, flat finish. A revolving stage 14 which has a built-in heater and can move up and down is installed to the front of said finely polished surface 13. The portion of this stage 14 onto which the wafer is loaded is equipped with a thin flat plate 15 made of quartz in order to prevent direct contact between the wafer and the metal stage. In order to provide proper adhesion of the wafer to the stage, vacuum suction is applied to the wafer via the aforementioned thin flat plate 15.

<0013>

The loading and unloading of the wafer 21 onto the stage 14 is performed by a transport robot (not shown) via the transport window 17, which can be opened and closed, installed on one side of the treatment chamber 16 that encloses the stage. When this occurs, the stage is moved up and down in order to allow the wafer suction surface of the robot to make contact with the rear surface of the wafer. Furthermore, at the same time that the reactive gas passes from the aforementioned multiple gas delivery nozzles onto the wafer in a uniform and high-speed fashion, the gas-flow gap 22 between the wafer surface and the aforementioned finely polished surface is narrowed so that the active oxygen atoms, which have a short lifetime, can be effectively applied to the wafer surface as this reactive gas flows into the treatment chamber. While the wafer 21 turns due to the rotation of the stage during the treatment process, the ultraviolet light is irradiated over the total surface along with the delivery of the reactive gas in order to provide a uniform application.

<0014>

A duct 18 is installed within the aforementioned treatment chamber 16 for the discharge of residual ozone, which is converted to oxygen through the use of a resolving device 19 and is then emitted into the atmosphere along with air.

<0015>

<Effect of the Invention>

This invention provides latent heat of evaporation prior to the point at which added moisture makes contact with the surface of a wafer. Moreover, since a loss of latent heat due to the combination of ozone with moisture is prevented, there is no cooling effect from the water, and as a result, partial cooling of the wafer surface upon delivery of the reactive gas can be prevented to any great extent, making it possible to conduct a uniform resist removal treatment operation and provide an improvement in the level of throughput.

<Simple Explanation of the Drawing>

<Figure 1>

This is a conceptual diagram that is used for the purpose of explaining the embodiment of this invention.

<Explanation of Symbols>

- 1: Ozone generator
- 2: A-pipe
- 3: Water vapor delivery tank
- 4: Fixed-quantity supply device
- 5: Heater A
- 6: Water vapor (or water vapor containing hydrogen peroxide)
- 7: Ozone air stream
- 8: B-pipe
- 9: Gas delivery nozzles
- 10: Flat plate made of composite quartz
- 11: Low-pressure mercury lamps
- 12: Lamp housing
- 13: Polished surface
- 14: Stage
- 15: Thin flat plate made of quartz
- 16: Treatment chamber
- 17: Transport window
- 18, 20: Ducts
- 21: Wafer
- 22: Gas-flow gap

<Figure 1>

Figure 1